Title: The Effect of the Surrounding Medium and its Pressure on Data Obtained in Thermal Diffusivity Measurements Using the Flash Method

Authors: Daniela E. Stroe*, Peter S. Gaal**

* Anter Laboratories, Inc., 1700 Universal Road, Pittsburgh PA, 15235, USA

(to whom further correspondence should be addressed)

** Anter Corporation, 1700 Universal Road, Pittsburgh PA, 15235, USA

Abstract

This work describes experimental measurements made with a high temperature – high pressure flash thermal diffusivity instrument, using nitrogen, argon and helium as environment. Data was generated using pressures from vacuum to 30 bar in the temperature range of ambient to 1000 ^{o}C. NIST SRM 8425 (Poco AXM 5Q, fine grain graphite) was used for the tests. A total of 2,970 data points were obtained, showing a clear and prominent shift in the data, depending on the pressure and the thermal properties of the surrounding gas. Preliminary conclusions drawn from the work indicate the influence of heat conduction, convection and diffusion through the environmental gas, on the thermal diffusivity results.

Key Words: thermal diffusivity, flash method, losses, high pressure, atmosphere

Introduction

The thermal diffusivity, α, of a medium is the thermophysical property that determines the speed of heat propagation by conduction during changes of temperature with time. The flash method, which is one of the most common ways to measure it, is based on depositing a very short energy pulse on the front face of a small disc shaped sample, and calculating its thermal diffusivity from the characteristic curve (thermogram) of the temperature excursion of its rear face.

The basic, analytical solution was first derived by Parker [1], who found that, for ideal conditions, the thermal diffusivity of the material can be calculated from:

$$\alpha = 0.1388 \frac{L^2}{t_{1/2}} \qquad (1)$$

where L is its thickness and $t_{1/2}$ is a characteristic time on the thermogram, when the rear surface reaches one half of its final temperature. Numerous corrections have been introduced to account for radiative heat losses during the process, the finite width of the laser pulse, and other factors interfering with the experiment, to more realistically represent actual experimental conditions. The method has been amply described in the literature [1-10]. The equipment used in the present work and its characteristics have been presented earlier [11], as a first part of a three phase project. The current work represents the second phase.

In the past, little or no attention was paid to the role the environmental gas (or vacuum, if that was the case) played in the resultant thermal diffusivity data. In most cases, 2…3 % variation in the results was considered to be within the experienced noise band of a ± 5 % of measured value. This study uncovered a definite influence of the type of gas used as atmosphere for the experiments and its pressure, on the measured thermal diffusivity values.

Experimental

The graphite reference material SRM 8425 was tested in 100 ^{o}C increments, in argon, nitrogen, helium and vacuum, from room temperature to 1000 ºC. For each type of gas used, the pressure inside the furnace was varied from 1, to 10, 20 and 30 bar. All other test parameters were kept the same in all cases, and the same procedure was followed for all the measurements.

Upon reaching thermal equilibrium, the pulse was applied and the data was recorded. Immediately thereafter, the basic Parker analysis and nine selected corrections (Koski, Heckman, Cowan (for two partial time ratios), Clark and Taylor (for three partial time ratios), Degiovanni (for two partial time ratios)) were calculated. The software is able to apply several additional corrections, as well as a regression analysis amongst them, named “goodness of fit”, to determine which correction provides the closest results to the ideal ones. For this study, the Clark and Taylor method of correcting the results was chosen, based on the best agreement between the experimental and the theoretical values, obtained at all instances. The thermal diffusivity values obtained using three different ratios of partial times were averaged and considered results of the measurements.

However, at elevated pressures, none of the existent corrections could account for the effect of the particular type of heat transport present.

A total of 54 tests were performed: 24 in nitrogen, 12 in argon, 6 in helium and 12 in vacuum, producing 2,970 data points. The relative standard deviation of the mean values of the thermal diffusivity results ranged between 0.1 and 0.5 % [12], the larger values corresponding to temperatures lower than 200 ^{o}C. This was expected, due to the extremely high variability of thermal conductivity of graphite around room temperature [13].

The results are combined and showed in table I, which gives an overview of all the average values obtained over the entire temperature and pressure range (including vacuum) for argon, nitrogen and helium. Incremental differences are calculated between the thermal diffusivity values obtained for each atmospheric pressure and vacuum. The differences are presented in units of cm^2/s, and also normalized, in percents of measured value. Data for helium at 1000 ^{o}C is not included, due to the inability of the furnace to reach the highest temperature with this type of atmosphere.

The data listed in the "average" columns is plotted in figure 1, showing a clear dependence on the nature of the gas, as well as a hint of some pressure dependence.

Table I Combined thermal diffusivity results for NIST SRM 8425

Temp. (ºC)	Press. (bar)	Average Th. Diff. (Argon) (cm^2/s)	Increm. Difference (Argon) (cm^2/s)	Increm. Difference (Argon) (%)	Average Th. Diff. (Nitrogen) (cm^2/s)	Increm. Difference (Nitrogen) (cm^2/s)	Increm. Difference (Nitrogen) (%)	Average Th. Diff. (Helium) (cm^2/s)	Increm. Difference (Helium) (cm^2/s)	Increm. Difference (Helium) (%)
25	0	0.8229			0.8229			0.8229		
25	1	0.8183	-0.0046	-0.56	0.7872	-0.0358	-4.54	0.8270	0.0041	0.49
25	10	0.8205	-0.0024	-0.29	0.7918	-0.0311	-3.93	0.8302	0.0073	0.88
25	20	0.8102	-0.0127	-1.57	0.7820	-0.0409	-5.24	0.8300	0.0070	0.85
25	30	0.8125	-0.0104	-1.29	0.7844	-0.0385	-4.91	0.8092	-0.0138	-1.70
100	0	0.6384			0.6384			0.6384		
100	1	0.6304	-0.0081	-1.28	0.6260	-0.0124	-1.98	0.6280	-0.0105	-1.66
100	10	0.6403	0.0019	0.29	0.6305	-0.0079	-1.25	0.6297	-0.0087	-1.38
100	20	0.6428	0.0044	0.68	0.6336	-0.0048	-0.76	0.6299	-0.0085	-1.35
100	30	0.6437	0.0053	0.82	0.6340	-0.0044	-0.70	0.6273	-0.0111	-1.77
200	0	0.4948			0.4948			0.4948		
200	1	0.4787	-0.0161	-3.37	0.4713	-0.0235	-4.98	0.4720	-0.0228	-4.84
200	10	0.4821	-0.0127	-2.63	0.4755	-0.0193	-4.07	0.4739	-0.0209	-4.42
200	20	0.4866	-0.0082	-1.68	0.4818	-0.0130	-2.69	0.4755	-0.0193	-4.06
200	30	0.4918	-0.0030	-0.60	0.4860	-0.0088	-1.81	0.4746	-0.0202	-4.26
300	0	0.3960			0.3960			0.3960		
300	1	0.3758	-0.0202	-5.38	0.3708	-0.0252	-6.78	0.3685	-0.0275	-7.45
300	10	0.3779	-0.0181	-4.79	0.3743	-0.0217	-5.81	0.3704	-0.0256	-6.91
300	20	0.3828	-0.0132	-3.44	0.3798	-0.0162	-4.26	0.3736	-0.0224	-6.00
300	30	0.3876	-0.0084	-2.17	0.3866	-0.0094	-2.43	0.3751	-0.0210	-5.59
400	0	0.3242			0.3242			0.3242		
400	1	0.3092	-0.0150	-4.84	0.3057	-0.0185	-6.07	0.3038	-0.0204	-6.73
400	10	0.3106	-0.0136	-4.38	0.3083	-0.0159	-5.15	0.3040	-0.0203	-6.66
400	20	0.3144	-0.0098	-3.11	0.3126	-0.0116	-3.71	0.3044	-0.0198	-6.50
400	30	0.3183	-0.0059	-1.84	0.3176	-0.0066	-2.08	0.3071	-0.0171	-5.56
500	0	0.2720			0.2724			0.2724		
500	1	0.2634	-0.0086	-3.27	0.2619	-0.0105	-4.00	0.2571	-0.0153	-5.96
500	10	0.2649	-0.0071	-2.70	0.2638	-0.0086	-3.26	0.2595	-0.0129	-4.98
500	20	0.2670	-0.0021	-0.80	0.2668	-0.0014	-0.53	0.2610	-0.0114	-4.36
500	30	0.2699	-0.0021	-0.79	0.2710	-0.0014	-0.52	0.2610	-0.0114	-4.35
600	0	0.2379			0.2379			0.2379		
600	1	0.2319	-0.0060	-2.60	0.2291	-0.0088	-3.85	0.2289	-0.0090	-3.95
600	10	0.2312	-0.0068	-2.92	0.2311	-0.0068	-2.96	0.2270	-0.0109	-4.82
600	20	0.2315	-0.0064	-2.78	0.2343	-0.0036	-1.55	0.2310	-0.0069	-2.99
600	30	0.2365	-0.0014	-0.61	0.2362	-0.0017	-0.72	0.2309	-0.0070	-3.05
700	0	0.2141			0.2141			0.2141		
700	1	0.2065	-0.0076	-3.69	0.2049	-0.0092	-4.49	0.1997	-0.0144	-7.22
700	10	0.2077	-0.0064	-3.06	0.2063	-0.0079	-3.81	0.2025	-0.0116	-5.75
700	20	0.2084	-0.0057	-2.71	0.2076	-0.0065	-3.15	0.2046	-0.0095	-4.63
700	30	0.2106	-0.0036	-1.69	0.2106	-0.0035	-1.67	0.2064	-0.0077	-3.75
800	0	0.1926			0.1926			0.1926		
800	1	0.1879	-0.0047	-2.48	0.1854	-0.0072	-3.91	0.1847	-0.0080	-4.31
800	10	0.1880	-0.0046	-2.45	0.1865	-0.0062	-3.30	0.1849	-0.0077	-4.16
800	20	0.1892	-0.0034	-1.82	0.1874	-0.0052	-2.78	0.1845	-0.0081	-4.38
800	30	0.1902	-0.0024	-1.26	0.1889	-0.0037	-1.98	0.1851	-0.0075	-4.08
900	0	0.1757			0.1757			0.1757		
900	1	0.1726	-0.0031	-1.79	0.1704	-0.0053	-3.13	0.1690	-0.0067	-3.96
900	10	0.1733	-0.0025	-1.41	0.1712	-0.0045	-2.61	0.1697	-0.0060	-3.53
900	20	0.1746	-0.0012	-0.66	0.1726	-0.0031	-1.80	0.1708	-0.0049	-2.89
900	30	0.1744	-0.0013	-0.75	0.1730	-0.0027	-1.54	0.1716	-0.0041	-2.38
1000	0	0.1630			0.1630					
1000	1	0.1601	-0.0030	-1.84	0.1579	-0.0051	-3.25			
1000	10	0.1608	-0.0022	-1.36	0.1591	-0.0039	-2.43			
1000	20	0.1611	-0.0019	-1.18	0.1591	-0.0039	-2.44			
1000	30	0.1612	-0.0018	-1.13	0.1609	-0.0021	-1.30			

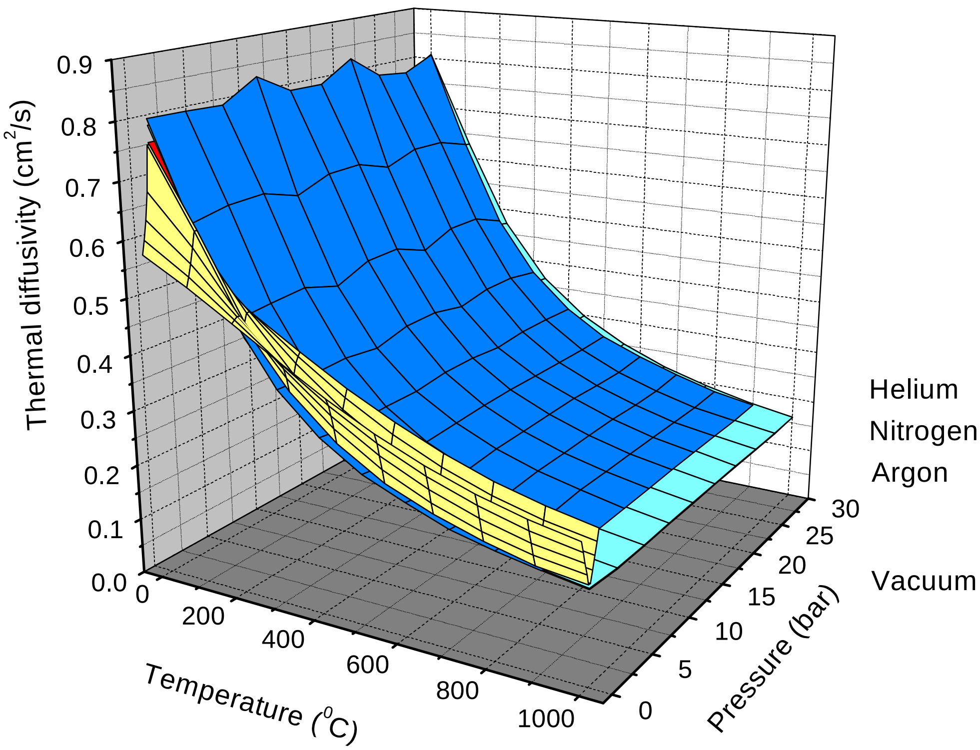

Figure 1. *Combined thermal diffusivity results for NIST SRM 8425*

Each surface shown in figure 1 represents the overall behavior in each particular gas. (In order to include on the plot the vacuum data, which is the base line, a nominal, very narrow pressure range was assigned to it.)

The surfaces created by the sets of data overlap, and it appears that they do not differ too much from each other. This is in line with currently prevalent interpretation in thermal diffusivity investigations where no provision is made to account or even acknowledge the existence of media dependent functionality. However, a more detailed approach reveals a consistent dependency of the results on the type of gas used, and on its pressure. This is a new concept, which becomes visible only if very small differences can be resolved by the equipment. When the differences between the curves are analyzed in terms of incremental variations of thermal diffusivity obtained from vacuum to each individual pressure, the changes are substantially magnified. Plotting them as a function of temperature, and with pressure as a parameter in similar three-dimensional form, yields figure 2.

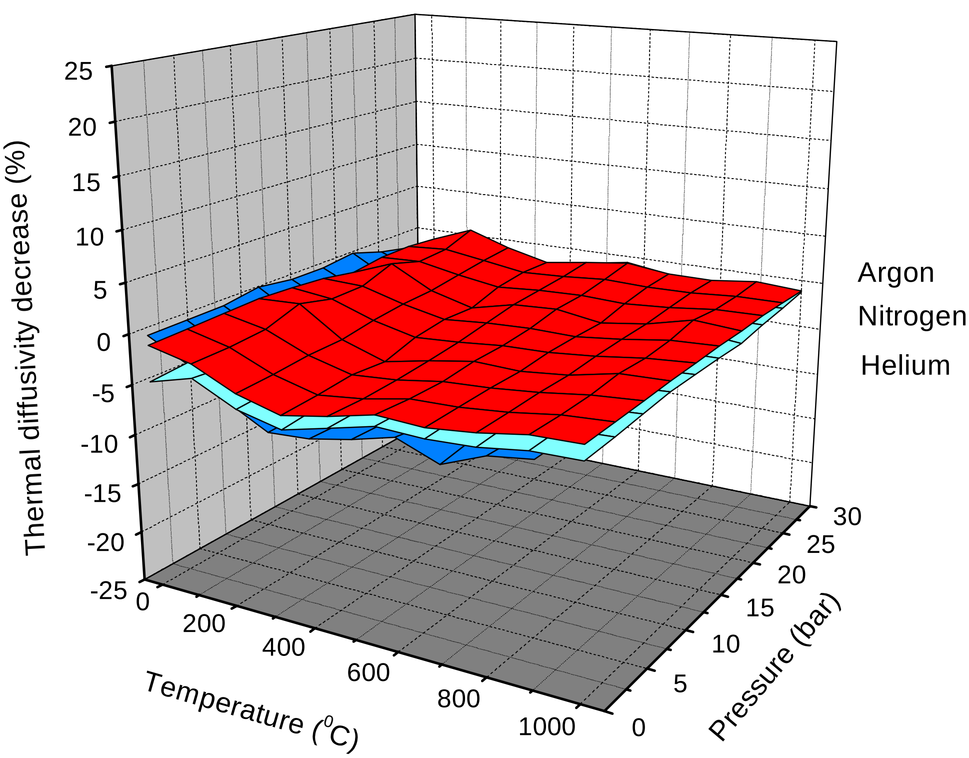

Figure 2 *Combined incremental changes for NIST SRM 8425*

The pressure dependence, as well as the dependence on the nature of the gas is clearly visible, while neither of those two, when expressed in incremental units, seems to change substantially with temperature. This suggests that one might squeeze each surface into a representative line (by averaging all temperature points for a particular gas) at each incremental pressure point. Then, summarizing the results from table I in this format, the incremental differences can be further averaged to give an overall view of the variations of the measured thermal diffusivity with pressure for each type of gas used, now referenced to the values obtained for vacuum. Table II shows the averaged incremental differences:

Table II Average incremental thermal diffusivity differences versus pressure, referenced to vacuum, for NIST SRM 8425

Pressure	Average Incremental Thermal Diffusivity Differences (%)		
(bar)	Argon	Nitrogen	Helium
0 (vacuum)	0	0	0
1	-2.83	-4.27	-4.56
10	-2.34	-3.51	-4.17
20	-1.73	-2.63	-3.63
30	-1.03	-1.79	-3.65

This, then, can be further represented in a more conventional graphical form, as shown in figure 3. Second order polynomial curves were fit to the points obtained for each type of gas.

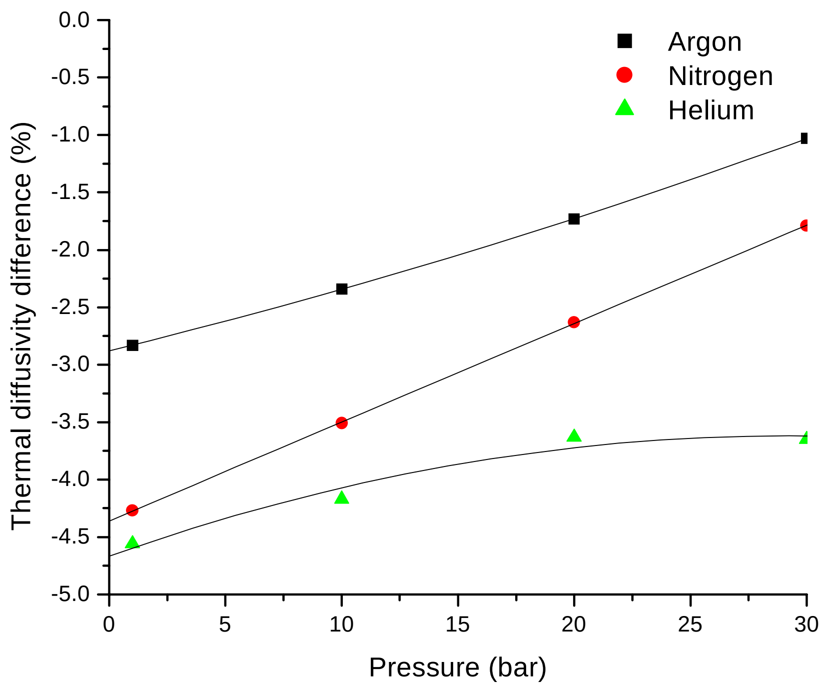

Figure 3 *Average of the incremental differences of thermal diffusivity, as a function of pressure, for NIST SRM 8425*

The results of this analysis indicate clearly the dependence of measured values on the surrounding medium. Earlier metrological validation process [12] has shown that the combined standard uncertainty associated with the thermal diffusivity values generated using this equipment is 1.13 %. Therefore, the systematic trends shown in figure 3 are considered significant and real.

Conclusions

This work shows that there is a definite dependence of the thermal diffusivity results on the nature of the environment in which the measurements are conducted. Since pressurization was found to have profound effects on the results, it is concluded that the process may be influenced not only by the radiative heat losses present in the thermal diffusivity experiment, but also by the heat conduction, convection, and thermal diffusion present into the surrounding gas. While no numerical or analytical relationships were established in the present study to concisely describe this relationship, the existence of this systematic behavior has been well indicated. The work is continuing on, in an attempt to link thermal conductivity, specific heat capacity, and density of the surrounding medium to a practically useful loss factor for measurements.

Bibliography

1. Parker, W. J., R. J. Jenkins, C. P. Butter, and G. L. Abbott, “Flash Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity”, *J. Appl. Phys.* **32**, p. 1679 (1961).
2. Clark, L. M. III and R. E. Taylor, “Radiation Loss in the Flash Method for Thermal Diffusivity”, *J. Appl. Phys.* **46**, p. 714 (1975).

3. Taylor, R. E. and L. M. Clark, III, “Finite Pulse Time Effects in Flash Diffusivity Method”, *High Temperatures – High Pressures* **6**, p. 65 (1974).

4. Taylor, R. E. and J. A. Cape, “Finite Pulse-Time Effects in the Flash Diffusivity Technique”, *Appl. Phys. Lett.* **5** (10), p. 210 (1964).

5. Cowan, R. D., “Pulse Method of Measuring Thermal Diffusivity at High Temperatures”, *J. Appl. Phys.* **34**, p. 926 (1963).

6. Cape, J. A. and G. W. Lehman, “Temperature and Finite Pulse-Time Effects in the Flash Method for Measuring Thermal Diffusivity”, *J. Appl. Phys* **34**, p. 1909 (1963).

7. Azumi, T. and Y. Takahashi, “Novel Finite Pulse-Width Correction in Flash Thermal Diffusivity Measurement”, *Rev. Sci. Instrum.* **52** (9), p. 1411 (1981).

8. Heckman, R. C., “Error Analysis of the Flash Thermal Diffusivity Technique”, in *Proceedings 14th International Thermal Conductivity Conference*, Plenum Press, New York (1976).

9. Koski, J. A., “Improved Data Reduction Method for Laser Pulse Diffusivity Determination with the Use of Minicomputers”, in *Proceedings of the 8th Symposium on Thermophysical Properties*, **2**, The American Society of Mechanical Engineers, p. 94, New York (1981).

10. Degiovanni, A., “Correction de longueur d’impulsion pour la mesure de la diffusivity thermique par la methode flash”, *Int. J. Heat Mass Transfer,* **31** (3), p. 2199 (1988).

11. Gaal, P. S., D. E. Apostolescu, “Thermal Diffusivity of Porous Carbon at High Pressures”, presented at The 15th European Conference on Thermophysical Properties, Wurzburg, Germany, September 1999 (in publication).

12. Stroe, D. E., A. Millea, Metrological Evaluation of a High Temperature Laser Flash Thermal Diffusivity Instrument, presented at The 14th Symposium on Thermophysical Properties, Boulder CO, June 2000.

13. “Standard Reference Materials: A Fine-Grained, Isotropic Graphite for Use as NBS Thermophysical Property RM’s from 5 to 2500 K”, NBS Special Publication 260-89, Gaithersburg (1984).